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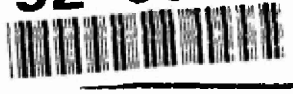

13. ABSTRACT *(Maximum 200 words)*

Effects of cyclodextrins on various families of laser dyes were studied. Unsubstituted as well as substituted cyclodextrins were examined in aqueous solutions. Among the laser dyes examined were examples of rhodamines, coumarins, bimanes, pyrromethene BF2 complexes, phenyl substituted oxazoles and p-terphenyl. Variable effects of the cyclodextrins were noted on the fluorescence and UV absorption of these dyes. The solubility of these compounds in aqueous solution was increased by the presence of cyclodextrins. Effects of cyclodextrins on lasing were also studied. Co-inclusion of amphiphiles together with laser dyes in the beta-cyclodextrin cavity was not found to have any significant effect on fluorescence emission. Infra red studies were performed on cyclodextrin solid complexes with coumarins. The presence of cyclodextrins in the mobile phase increased the retention factor values for many dyes on thin layer chromatography. Extraction of laser dyes from aqueous solutions with solid phase cyclodextrin cartridges was also done.

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CYCLODEXTRIN INCLUSION COMPLEXES WITH BIMANES AND OTHER LASER DYES

FINAL REPORT

INCORPORATING THE REPORT FOR THE PERIOD
1 JANUARY 1991 - 30 JUNE 1991

DR. IEVA R. POLITZER

JULY 9, 1991

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XAVIER UNIVERSITY OF LOUISIANA

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TABLE OF CONTENTS:

LIST OF FIGURES AND TABLES

STATEMENT OF THE PROBLEM STUDIED

During the course of this project, we studied the effects of cyclodextrins on various families of laser dyes. Alpha, beta, and gamma cyclodextrins as well as numerous substituted cyclodextrins were examined in aqueous solutions. Among the laser dyes examined were the xanthene dyes including rhodamines 6G,B, S101, sulforhodamine B and the disodium salt of fluorescein; the coumarin dyes 30, 314, 314T, 102, 153, 7-hydroxycoumarin and the salts of 7-hydroxy-4-methylcoumarin; a number of syn- and anti-bimane dyes; two pyrromethene BF2 complexes; some phenyl substituted oxazoles and p-terphenyl. The effects of the cyclodextrins were noted on the fluorescence and UV absorption of these dyes in aqueous solutions. These effects were found to be variable, depending not only upon the compound being examined, but its concentration in solution as well. Almost invariably, the solubility of these compounds in aqueous solution was increased by the presence of cyclodextrins. Effects of cyclodextrins on lasing were studied for some rhodamines, coumarins and pyrromethene BF_2 complexes. The lasing was greatly increased for some rhodamines, but not much affected for the latter two families of dyes. Possible co-inclusion of amphiphiles together with selected laser dyes in the beta-cyclodextrin cavity was not found to have any significant effect on fluorescence emission as long as increased solubility effects were rigorously excluded. Infra red studies were performed on cyclodextrin solid complexes with coumarins and a shift of the carbonyl absorption was found in some cases. Thin layer chromatography of the various laser dyes and some dye analogs revealed that in many instances, the presence of cyclodextrins in the mobile phase greatly increased the retention factor values and could prove valuable in the separation and purification of these dyes. Studies were also carried out on the extraction of laser dyes from aqueous solutions with solid phase extraction cyclodextrin cartridges.

SUMMARY OF THE MOST IMPORTANT RESULTS

1. STABILITY OF CYCLODEXTRINS IN AQUEOUS SOLUTIONS

The stability of various cyclodextrins (CDs), 10^{-2}M, in aqueous solutions, was monitored by UV absorbance over a two week period. The pH of these freshly prepared solutions was also measured. All three unsubstituted CDs, alpha, beta and gamma, were examined, as well as the substituted CDs, hydroxyethyl, hydroxypropyl, dimethyl, trimethyl and triacetyl. In contrast to the unsubstituted CDs, which are single products, the substituted CDs typically contain numerous homologs and isomers of the products that are symmetrically distributed around an average molecular mass. The structure and dimensions of beta cyclodextrin (B-CD) are shown in Fig. 1.

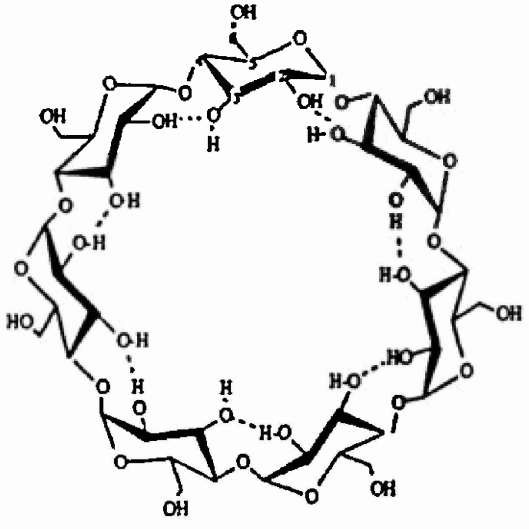
The UV results are summarized in Table 1. As noted in the Table, alpha and gamma CDs show no absorption. Beta CD and the substituted beta CDs show some absorption; the absorption is very weak for hydroxyethyl-B-CD, M31 and triacetyl-B-CD. Only unsubstituted B-CD shows a significant blue shift with time over a two week period. In general, aged aqueous solutions of B-CD (solutions one week old or older) show a λmax 255-265 nm. However, freshly prepared aqueous solutions of B-CD show λmax 278 nm on the first day. The rate of shift of the absorption appears to be somewhat pH dependent. Strongly acidic or basic soutions shift slowly and near-neutral solutions shift within one day. Heating (70 - 80°C) of the 10^{-2}M B-CD solutions did not appear to influence the rate of the shift from longer to shorter wavelength absorption.

To examine the effects of pH on B-CD, aliquots of water were adjusted to pH 2.01, 4.06, 6.42, 7.53 and 9.92 and then made 10^{-2} M by adding solid B-CD. The pH was then reread and was monitored throughout the study without any further adjustments. The addition of B-CD did not significantly alter the pH of acidic to neutral solutions. However, addition of B-CD to basic solutions resulted in a marked decrease of pH. Some subsequent drifting of pH with time was often observed. The pH was determined for freshly prepared solutions, 10^{-2}M of the various CDs. Average pH values for these solutions are shown in Table 2 below. These solutions were monitored over a two week period and considerable drifting of pH with time was observed over a range of 7.2 - 6.1 pH.

The behavior of B-CD was also examined in mixed solvents. Solubility and effects of time on UV absorption were considered. For the solubility study, 1.135 g of B-CD were placed in 100 ml of solvent (if dissolved, this would result in a 10^{-2} M solution). In pure methanol or ethanol, the B-CD was only partially soluble, even with warming. In ethanol:water (1:1), the B-CD dissolves at room temperature. In methanol:water or glycerol:water (1:1), B-CD dissolves only in warm solution and recrystallizes at room

temperature. For all of the above solutions, the UV absorption λmax 272-278 nm did not shift during a one week time period.

In all fluorescence studies involving the presence of CDs, the pertinent CD solution was examined for fluorescence activity under the same parameters as used for the guest compound. Without exception, none of the CDs utilized ever showed any fluorescence.



Chemical structure of β-cyclodextrin.

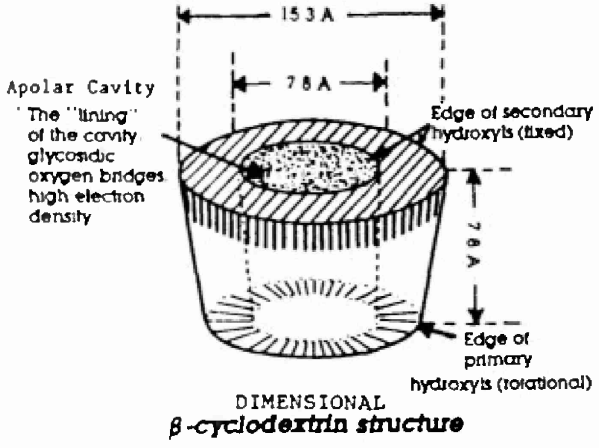


Fig. 1. Chemical and dimensional structure of beta-cyclodextrin

TABLE 1

UV absorption, λ max nm, of 10^{-2} M aqueous solutions of cyclodextrins (CDs)
(UV instrument set for high sensitivity)

TIME	α-CD	B-CD	γ-CD	HE-B-CD[a] MS1	HEBCD[a] MS1.6	HPBCD[b] MS0.6	HPBCD[b] MS0.9	diMeBCD[c]	triMeBCD[d]	triacetyl B-CD
1 day	--	278	--	weak absorpt. ~260	270	268	266	270	strong 360-200	weak absorpt. ~270
1 week	--	255-265	--	weak absorpt. ~260	265	270	265	270	strong 360-200	weak absorpt. ~260
2 weeks	--	255-265	--	weak absorpt. ~255	265	265	265	270	strong 360-200	weak absorpt. ~255

a. HE-B-CD MS=1 and MS=1.6: Hydroxyethyl-beta-cyclodextrin with average molecular substitution of 1 and 1.6 respectively

b. HP-B-CD MS=0.6 and MS=0.9: Hydroxypropyl-beta-cyclodextrin with average molecular substitution of 0.6 and 0.9 respectively

c. diMe-B-CD: Heptakis(2,6-di-O-methyl)-beta-cyclodextrin

d. tri Me-B-CD: Heptakis(2,3,6-tri-o-methyl)-beta-cyclodextrin

TABLE 2

pH of freshly prepared aqueous solutions of cyclodextrins (CDs), 10^{-2} M

CD:	α-CD	B-CD	γ-CD	HEBCD[a] MS1	HEBCD[a] MS1.6	HPBCD[b] MS0.6	HPBCD[b] MS0.9	diMeB-CD[c]	triMe-B-CD[d]	triacetyl CD	H_2O (no CD)
pH:	6.7	6.9	6.6	6.9	6.8	6.9	7.2	6.4	6.8	6.8	6.7

a. HE-B-CD MS=1 and MS=1.6: Hydroxyethyl-beta-cyclodextrin with average molecular substitution of 1 and 1.6 respectively

b. HP-B-CD MS=0.6 and MS=0.9: Hydroxypropyl-beta-cyclodextrin with average molecular substitution of 0.6 and 0.9 respectively

c. diMe-B-CD: Heptakis(2,6-di-O-methyl)-beta-cyclodextrin

d. tri Me-B-CD: Heptakis(2,3,6-tri-O-methyl)-beta-cyclodextrin

2. EFFECTS OF CYCLODEXTRINS ON SELECTED RHODAMINES AND THE DISODIUM SALT OF FLUORESCEIN

A study was done of the fluorescence and UV absorption of selectsd rhodamines and ths effects of the unsubstituted cyclodextrins (CDs), α-CD, β-CD, and γ-CD and the substitutsd CDs, hydroxyethyl, hydroxypropyl and dimsthyl-B-CD. The rhodaminss selscted were RH 6G, Rh B, Rh S 101 and Rh S B.The structures of thess rhodamines are shown in Fig.2. The results for fluorescence emission and UV absorption are summarized in Table 3 and Table 4 rsspectively.

As seen in Table 3, all CDs induced an enhancement of fluorescence for concentrated (10^{-3} M) aqueous solutions of the rhodamines. Among the CDs, dimethyl-B-CD and the hydroxypropyl-B-CDs induced a greatsr fluorescence enhancement than B-CD. Somswhat surprisingly, gamma CD, which becauss of its larger cavity diamster might have been expected to have the greatest sffsct on fluorescence, was overshadowed as a fluorescence enhancsr by dimethyl-B-CD. We also note that for Rh B, the results obtained for a .5 x 10^{-3} M solution paralelled those obtained for the 1 x 10^{-3} M solution in terms of relativs CD sffects on fluorescence.

Further dilution, howsver, can change the effects of B-CD on the fluorescence of Rh 6 G and Rh B as well as ths disodium salt of fluorescein. Thsss rssults, covering a dye concentration range of 10^{-3} to 10^{-8} M, are presented in Tabls 5 and have bsen published by us (1). As shown in this tabls, addition of B-CD to sequentially diluted solutions of thess xanthene dyes has variable effects on fluorescsnce. B-CD can inducs sithsr snhancement or quenching depending on the nature and concentration of ths dye. Thess changes in the effects of B-CD on dilute solutions (10^{-5} to 10^{-8} M) of xanthene dyes may reflsct the formation of different types of concentration dependent inclusion complsxes betwsen the dyes and B-CD.

For concentrated (10^{-3} M) solutions of the Rhodamine dyes, Rh 6 G, Rh B, S Rh 101 and S Rh B, all of the CDs examined induced a quench of ths shorter wavelsngth absorption and enhanced or did not affect the longer wavelength absorption. (Tabls 4). This was also the observation for a 0.5 x 10^{-3} M solution of Rh B. Ths effects of B-CD were also examinsd for mors dilute solutions (10^{-4} to 10^{-7} M) of Rh 6 G and Rh B as wsll as for the disodium salt of fluorescein over the concentration range of 10^{-3} M to 10^{-6} M. These results have besn describsd in our rscent publication (1). In this dilution range, considerable differences in ths effscts of B-CD were observed not only from dye to dye, but also depending upon the concentration of the dye. For ths disodium salt of fluorescein, strong quenching of absorption by B-CD was observed over the entire indicated dye concentration range.

Rh 6 G (10^{-4} to 10^{-7} M) showed a small absorption enhancement upon addition of B-CD as well as a slight red shift. The effect of B-CD on the absorption of Rh B varied with the concentration of the dye. A quench was indicated in 10^{-5} and 10^{-6} M solutions and a slight absorption enhancement in 10^{-7} M solutions. Monitoring pH ascertained that these absorption changes were not pH induced.

The lasing of the xanthene dyes Rh 6 G, Rh B and the disodium salt of fluorescein (10^{-3} M aqueous solutions) was examined using a flashlamp pumped dye laser. These results have been published by us and are presented in Table 6 (1). It is noted that in studies using nitrogen lasers, no lasing was reported for Rh B or Rh 6 G in aqueous solutions. In our studies, the lasing for all three dyes (10^{-3} aqueous solutions) was enhanced in the presence of 10^{-2} M B-CD. The most dramatic effect was for RhB and the smallest effect was observed for the disodium salt of fluorescein.

TABLE 3

Effects of cyclodextrins (10^{-2} M) on the fluorescence emission of Rhodamine 6G, Sulforhodamine 101, Rhodamine B, and Sulforhodamine B in aqueous solutions (Cyclodextrin induced percent enhancement)

Dye	α-CD	β-CD	γ-CD	dimethyl-β-CD	HE-β-CD MS=1	He-β-CD MS=1.6	HP-β-CD MS=0.6	HP-β-CD MS=0.9
Rh 6G 10^{-3}M λ_{em} 591nm	71	322	452	554	235	184	388	345
S Rh 101 10^{-3}M λ_{em} 641nm	19	37	135	209	101	150	118	156
Rh B 10^{-3} M 0.5×10^{-3}M λ_{em} 603nm	214 102	494 150	74 32	688 210	569 128	563 143	687 165	757 182
S Rh B 10^{-3}M λ_{em} 623nm	70	355	152	376	329	309	386	381

HE-β-CD MS=1 and MS=1.6: Hydroxyethyl-beta-cyclodextrin with average molecular substitution of 1 and 1.6 respectively

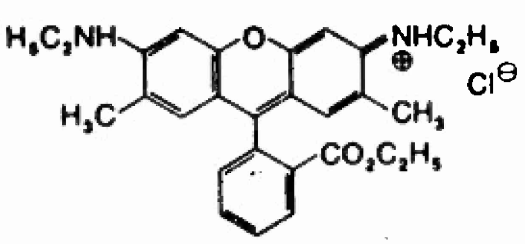
HP-β-CD MS=0.6 and MS=0.9: Hydroxypropyl-beta-cyclodextrin with average molecular substitution of 0.6 and 0.9 respectively

dimethyl-β-CD: Heptakis(2,6-di-O-methyl)-beta-cyclodextrin

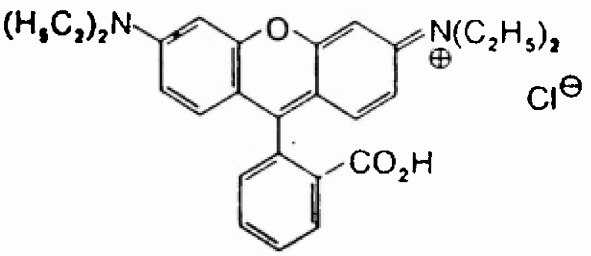
$$\text{CD induced \% enhancement} = \frac{\text{relative fluorescence intensity of rhodamine + CD} - \text{relative fluorescence intensity of rhodamine}}{\text{relative fluorescence intensity of rhodamine}} \times 100\%$$

FIG.2. STRUCTURES OF SELECTED RHODAMINES

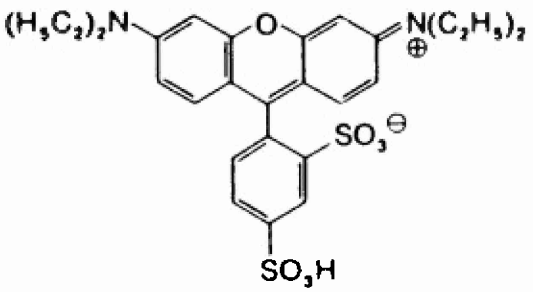
Rhodamine 6G



Rhodamine B



Sulforhodamine B



Sulforhodamine 101

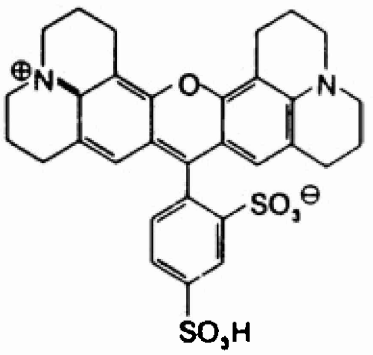


TABLE 4

Effects of cyclodextrins (10^{-2}M) on the UV absorption of rhodamine 6G, sulforhodamine 101, rhodamine B and sulforhodamine B in aqueous solutions.

Dye	α-CD	β-CD	γ-CD	dimethyl β-CD	HE-β-CD MS=1	HE-β-CD MS=1.6	HP-β-CD MS=0.6	HP-β-CD MS=0.9
Rh 6G, 10^{-3}M λ max 500 nm λ max 526 nm	quench enh	quench enh	quench enh	quench enh	quench enh	quench enh	quench enh	quench enh
S Rh 101, 10^{-3}M λ max 549 nm λ max 585 nm	sl. quench same	sl. quench same	sl quench same	quench sl. enh	quench sl. enh	quench sl. enh	quench sl. enh	quench sl. enh
Rh B, .5x10^{-3}M sh 522 nm λmax 553 nm	quench enh	quench enh	quench enh	quench enh	quench enh	quench enh	quench enh	quench enh
S Rh B, 10^{-3}M λ max 530 nm λ max 564 nm	quench sl. enh	quench sl. enh	quench sl. enh	quench sl. enh	quench sl. enh	quench sl. enh	quench sl. enh	quench sl. enh

HE-β-CD MS=1 and MS=1.6: Hydroxyethyl-beta-cyclodextrin with average molecular substitution of 1 and 1.6 respectively

HP-β-CD MS=0.6 and MS=0.9: Hydroxypropyl-beta-cyclodextrin with average molecular substitution of 0.6 and 0.9 respectively

dimethyl-β-CD: Heptakis(2,6-di-O-methyl)-beta-cyclodextrin

TABLE 5

Effect of β-cyclodextrin (10^{-2} M) on the fluorescence emission of rhodamine 6G, the disodium salt of fluorescein and rhodamine B in aqueous solutions

Dye conc. (M)	Rh B		Rh 6G		Fl-di-Na	
	λ_{em} (nm) (λ_{ex} = 500 nm)	effect of B-CD (factor) [a]	λ_{em} (nm) (λ_{ex} = 475 nm)	effect of B-CD (factor) [a]	λ_{em} (nm) (λ_{ex} = 450 nm)	effect of B-CD (factor) [a]
10^{-3}	613-624	enhance (7.9)	593-604	enhance (6.9)	535	enhance (1.5)
10^{-4}	587	quench (0.69)	566-568	enhance (1.9)	520	enhance (1.1)
10^{-5}	580	quench (0.59)	553	quench (0.92)	506	quench (0.82)
10^{-6}	574	quench (0.68)	548	quench (0.90)	503	quench (0.84)
10^{-7}	575	quench (0.67)	547	enhance (1.2)	504	quench (0.67)
10^{-8}	570	quench (0.76)	547	enhance (2.9)	500	quench (0.81)

[a] Factor = (peak height of dye + B-CD) / (peak height of dye).

TABLE 6

The lasing of 10^{-3} M aqueous solutions of rhodamine B, rhodamine 6G and the disodium salt of fluorescein in the presence and absence of 10^{-2} M β-cyclodextrin

Dye solution	Rh B lasing (kV)		Rh 6G lasing (kV)		Fl-di-Na lasing (kV)	
	threshold	intense	threshold	intense	threshold	intense
without B-CD	no lasing		15	18	12	14
with B-CD	11	14	8	12	11	13

Tables taken from our publication (1).

3. CYCLODEXTRIN EFFECTS ON SELECTED COUMARINS IN SOLUTION

The effects of B-CD and hydroxyethyl-B-CD on the "water insoluble" coumarins 102, 153, 30, 314, 314T, were studied as well as the effects of B-CD on the "water soluble" coumarins, 7-hydroxycoumarin (7(OH)C) and the Na and K salts of 7-hydroxy-4-methylcoumarin (7(OH)4(Me)C). The structures of these coumarins are shown in Fig. 3.

Coumarin solubility and UV absorption with various CDs:

For 1:1 aqueous ethanolic solutions of coumarins 102, 153, 314 and 314T, the intrinsic effect of B-CD (and hydroxyethyl-B-CD, average molecular substitution 1 and 1.6) is a quench of the UV absorbance. The absorbance is considerably lower than that obtained in pure ethanol. The solubility of all of these coumarins, in freshly prepared solutions, was increased in 10^{-2} B-CD (for coumarins 314 and 314T, also in hydroxyethyl-B-CD). Qualitatively, these effects prevailed upon aging (2 weeks), but quantitatively, the degree of change was variable with time. For coumarins 314 and 314T, fresh solutions showed the largest solubilizing effect with hydroxyethyl-B-CD, ave. mol. subst. 1. For coumarins 314 and 314T, coumarin concentrations as high as 10^{-3} M can be attained in slightly warm 1:3 EtOH:H_2O solutions which are 10^{-2} in B-CD. The UV absorption of coumarin 102 (maximum concentration, 10^{-5} M) in aqueous solution was not affected by 10^{-2} M B-CD. The solubility of coumarin 102 in water was increased in the presence of 10^{-2} M B-CD. These results have been published in part (2). The UV absorption of coumarin 314 T (max. conc. 10^{-5} M) in aqueous solution was increased in the presence of 10^{-2}M B-CD. The solubility of this compound was also increased by B-CD. The UV absorption of fresh aqueous solutions of coumarin 314, however, was quenched and red-shifted by B-CD.

Coumarin fluorescence with various CDs:

The fluorescence of 10^{-3} M solutions of coumarins 314 and 314T in 1:1 EtOH:H2O was not affected by B-CD (10^{-2} M). These solutions were monitored over a one week period. In 1:3 EtOH:H2O with 10^{-2} B-CD, the fluorescence of coumarin 314 is quenched as compared to ethanol. For coumarin 314T in the same medium, the fluorescence is initially quenched but then rises to the same intensity as in ethanol by day 3. The addition of small amounts of acid, (HCl) to aqueous ethanolic solutions of coumarins 314 and 314T does not have any major effect on the fluorescence. The fluorescence of 314 T (max. conc. 10^{-5}M) in aqueous solution was enhanced and blue shifted by 10^{-2}M B-CD. Fluorescence studies also confirmed increased solubility in aqueous B-CD. The fluorescence of 314, however, was quenched in fresh aqueous solution of 10^{-2}M B-CD.The fluorescence of coumarins 102 and

153 in water (maximum concentration, 10-7 M) was considerably enhanced by 10^{-2} M B-CD. The addition of B-CD showed a blue shift for the Em peaks and a slight shift for the Ex peaks. These results have been published in part (2).

Effect of B-CD on the lasing of coumarins 314 and 314T:

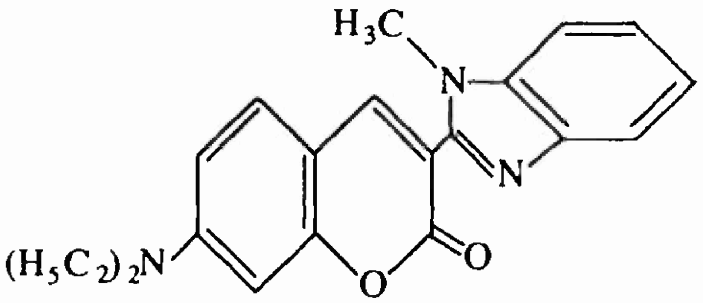
The lasing of coumarins 314 and 314T (10^{-3} M) was determined in ethanol and in ethanol-water solutions in the presence and absence of 10^{-2} M B-CD. The lasing was most efficient in ethanol and diminished in ethanol-water solutions. The addition of B-CD (10^{-2} M) appeared to even further diminish the efficiency of lasing for the ethanol-water solutions.

B-CD and the "water soluble" coumarins:

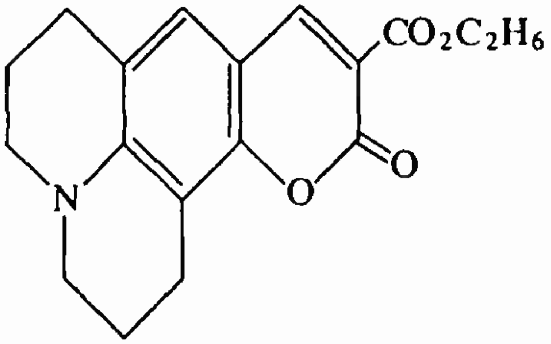
The effects of B-CD were examined on the fluorescence, UV and lasing of 7-hydroxycoumarin (7(OH)C) and the Na and K salts of 7-hydroxy-4-methylcoumarin, (7(OH)4(Me)C. These results are presented in detail in our publication (2), pp438 - 440. In summary, B-CD quenched the UV absorption of these compounds. B-CD enhanced the fluorescence of 7(OH)C and quenched the fluorescence of basic solutions of the K and N salts of 7(OH)4(Me)C for fresh solutions. With aging, solutions with B-CD show apparent enhancement. This is probably a protective effect by B-CD against decomposition rather than real enhancement.

The lasing of 7(OH)C was examined in the 450 - 473 nm range and B-CD was found to have no major effect on the lasing. The lasing of the K salt of 7(OH)4(Me)C was examined and B-CD was found to have no effect in concentrated solutions and was found to induce a slight quench in diluted solutions. In summary, the lasing in basic solutions is very pH sensitive for these compounds and B-CD has no major effect.

FIG 3. STRUCTURES OF SELECTED COUMARIN LASER DYES



Coumarin 30



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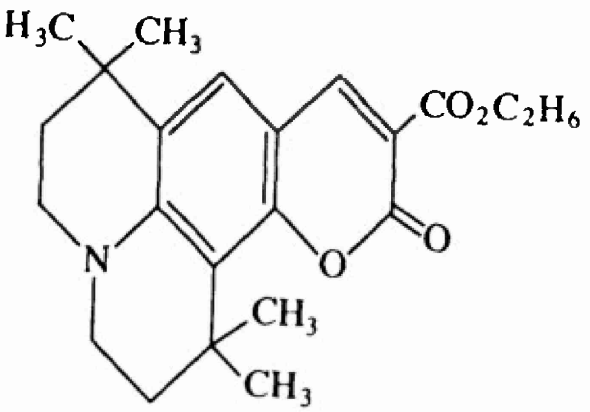
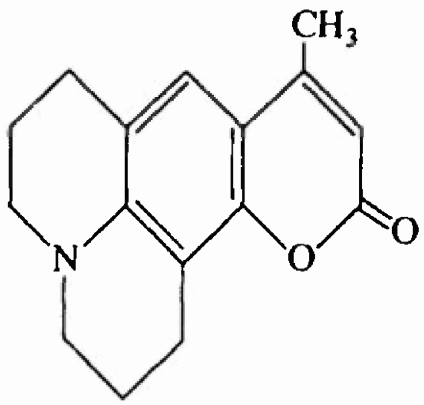
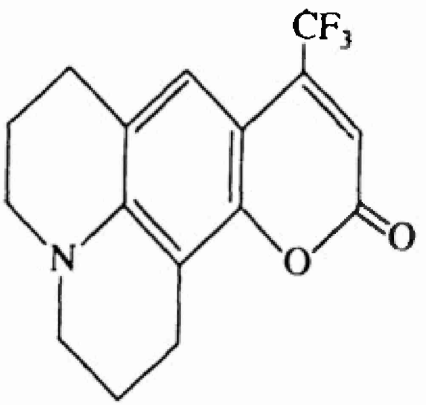


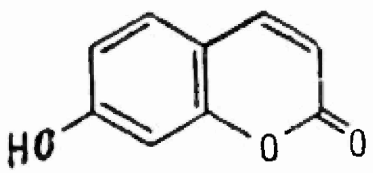
Coumarin 314T



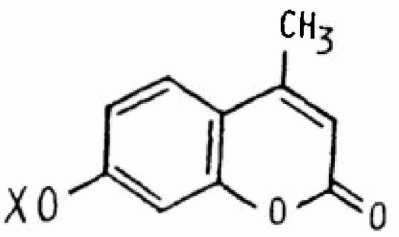
Coumarin 102



Coumarin 153



7-hydroxycoumarin



X =Na, K

salts of 7-hydroxy-4-methylcoumarin

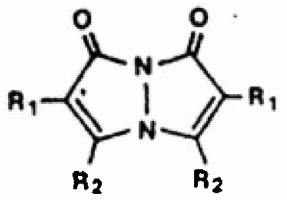
4. B-CYCLODEXTRIN AND BIMANES

The effects of B-cyclodextrin were investigated on the fluorescence emission and excitation as well as on the UV absorption and solubility of certain bimanes in aqueous solution. Three syn-bimanes with differing water solubilities were examined, namely, syn-(CH_2OCOCH_3, CH_3) bimane, syn-(CH_3, CH_3) bimane, and syn-(C_6H_5, Cl) bimane. The anti-(CH_3, CH_3) bimane was also examined. The structures of these bimanes are shown in Fig. 4. In dilute solutions, the syn-(CH_3, CH_3) bimane and syn-(C_6H_5, Cl) bimane showed enhancement of their relative fluorescence intensities upon the addition of B-cyclodextrin as did anti-(CH_3, CH_3) bimane. Only the anti-(CH_3, CH_3) bimane showed significant changes in its UV absorption upon the addition of B-cyclodextrin. Both syn-(CH_2OCOCH_3, CH_3) bimane and syn-(CH_3, CH_3) bimane solubilities were increased in the presence of B-CD. The formation of B-cyclodextrin inclusion complexes is proposed as a possible interpretation of these observations. These results have been presented in detail in our paper (3).

The effects of time and heat were examined on the B-CD induced fluorescence enhancement for syn-(CH_3, CH_3) bimane. Aliquots of 10^{-7} M solutions of this bimane both with and without 10^{-2} M B-CD were monitored over a two week period. In one series, solutions were also heated (twice, 80°C/1 hr.) during this period. Neither time nor heat induced any significant change in the fluorescence enhancement which was originally observed. Attempts to prepare a solid B-CD complex using syn-(CH_3, CH_3) bimane did not yield material containing bimane inclusion complex upon X-ray analysis.

syn-Bimanes

1 syn-(CH_2OCOCH_3, CH_3) bimane
2 syn-(CH_3, CH_3) bimane
3 syn-(C_6H_5, Cl) bimane



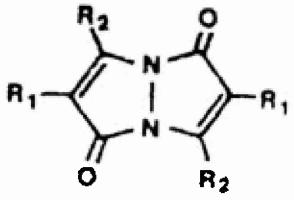
syn-(R_2.R_1) bimane

Compound	R_1	R_2
1	CH_3	CH_2OCOCH_3
2	CH_3	CH_3
3	Cl	C_6H_5

anti-Bimane

4 anti-(CH_3, CH_3) bimane

$R_1 = R_2 = CH_3$



anti-(R_2.R_1) bimane

FIG. 4. STRUCTURES OF SELECTED BIMANES

5. B-CYCLODEXTRIN AND PYRROMETHENE BF_2 COMPLEXES

B-CD was added to aqueous solutions of 1,3,5,7,8-pentamethyl pyrromethene-BF_2 (very water insoluble) and the disodium salt of 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-BF_2 complexes (compounds supplied by Dr. J. H. Boyer). The structures of these coumpounds are shown in Fig. 5. B-CD (10^{-2}M) induced fluorescence quenching for the former compound, but this effect can vary depending on the parameters used. For the latter compound, B-CD induces a very small enhancement (1-2%) of fluorescence emission and does not affect the UV absorption at λmax 490 nm. Aqueous 10^{-3} and 10^{-4} M solutions of this disodium salt lased in the range of 530-555 nm and B-CD (10^{-2}M) had no major effect on the lasing. The disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-BF_2 complex fluorescence changes with dilution from 10^{-3} to 10^{-8} M. Deaggregation in dilute solutions is suggested. These fluorescence results are presented in Table 7 and have been published by us (2).

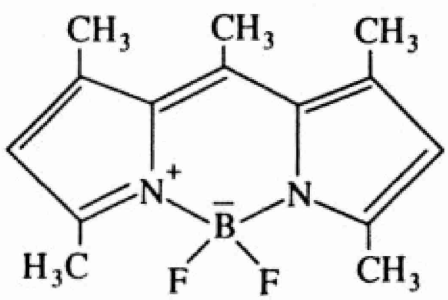
TABLE 7

Fluorescence of a sodium pyrromethene-BF_2 complex upon dilution

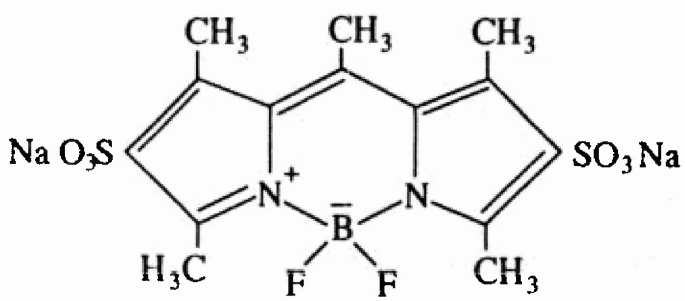
disodium 1,3,5,7,8-pentamethylpyrromethene-2, 6-disulfonate-BF_2 complex

Fluorescence in aqueous solutions

Molarity	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}
Em λmax, nm ex=404nm	534	524	517	513	509	509
Ex λmax, nm ex=534nm	404	444	484	486	486	486



1,3,5,7,8-pentamethylpyrromethene-BF_2 complex



disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-BF_2 complex

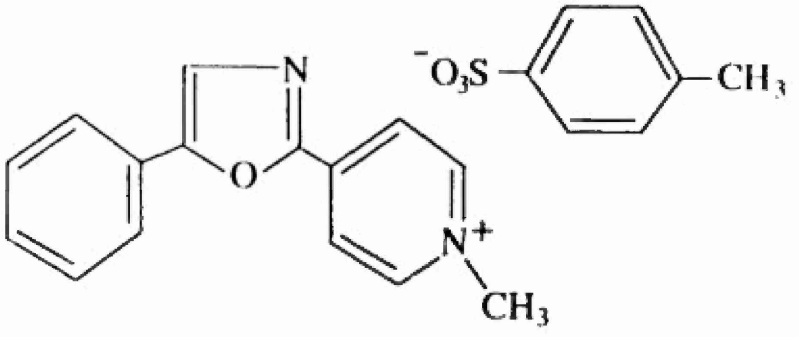
FIG. 5. STRUCTURES OF SELECTED PYRROMETHENE COMPLEXES

6. EFFECTS OF B-CYCLODEXTRIN ON THE FLUORESCENCE, UV ABSORPTION AND SOLUBILITY OF PHENYL SUBSTITUTED OXAZOLES AND TERPHENYL

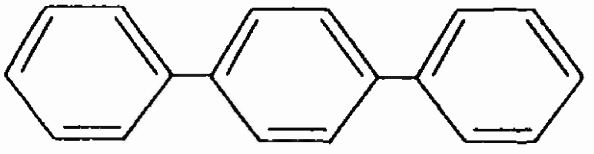
The fluorescence, UV absorption and solubility of four selected phenyl substituted oxazoles was investigated in ethanol:water (1:1) solutions, since these compounds were highly insoluble in purely aqueous solutions. In all cases investigated, B-CD increased the solubility of these compounds. The fluorescence emission was quenched by 10^{-2} M B-CD. The UV absorption was likewise quenched, except for POPOP, for which, depending upon the age of the solution, B-CD could induce either a quench or an enhancement. These results, together with the structures of the oxazoles investigated, are summarized in Table 8.

It is noted that for the phenyl oxazole salt, shown below, B-CD induces a shift and a small quench of UV absorption and also induces a small enhancement of fluorescence.

The UV absorption of terphenyl was determined in a 1:1 ethanol:water solution in the presence and absence of B-CD. The effect of B-CD (10^{-2}M) on the UV absorption of terphenyl is enhancement of absorbance. The solubility of terphenyl is also increased in the presence of B-CD, especially with time, over a period of two weeks. The structure of terphenyl is shown below.



phenyl oxazole salt

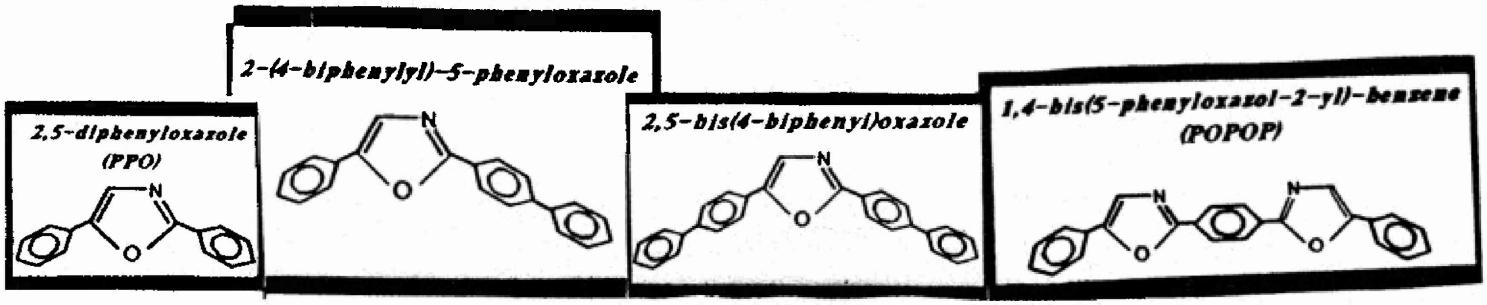


Terphenyl

TABLE 8

EFFECTS OF B-CYCLODEXTRIN ON THE FLUORESCENCE, UV ABSORPTION AND SOLUBILITY OF PHENYL SUBSTITUTED OXAZOLES

Structures of phenyl substituted oxazoles investigated:



UV Determination of intrinsic effects and solubility effects

of B-cyclodextrin in aqueous or ethanol/H_2O (1:1) systems.

Compound being studied	Intrinsic effect of B-cd	Solubility effect of B-cd
2,5-diphenyl oxazole (PPO) (H_2O) at λ = 280	quench	enhancement
2-(4-biphenyl)-5-phenyloxazole ($ETOH/H_2O$) at λ 324	quench	enhancement
2,5-bis-(4-biphenyl)oxazole) ($ETOH/H_2O$)	- No UV data available due to poor solubility -	
1,4-bis (5-phenyl oxazole-2-yl)-benzene (POPOP) ($ETOH/H_2O$) at λ = 360	enhancement	enhancement

Fluorescence Determination of Intrinsic Effects and Solubility

Effects of B cyclodextrin in Aqueous or Ethanol/H_2O(1:1) Systems

Compound being Studied	Intrinsic Effect of B-cd	Solubility Effect of B-cd
2,5-diphenyl oxazole (PPO) (H_2O) (10^{-4} M) λ exc 334 λ max 368-370	quench	enhancement
2-(4-biphenyl)-5-phenyl oxazole ($ETOH/H_2O$) (10^{-5} M) λ exc 358 λ max 390	quench	enhancement
2,5-bis-(4-biphenyl)oxazole ($ETOH/H_2O$) (10^{-5} M) λ exc 338 λ max 400-410	enhancement	enhancement
1,4-bis(5-phenyl oxazole-2-yl)-benzene (POPOP) ($ETOH/H_2O$) (10^{-3} M) λ exc 358 λ max 419-420	quench	enhancement

7. CO-INCLUSION OF AMPHIPHILES TOGETHER WITH SELECTED LASER DYES IN THE B-CYCLODEXTRIN CAVITY

The effects on fluorescence of the possible co-inclusion of ethsnol and/or methanol together with the guest compound in the B-CD cavity were examined for a series of laser dyes. With the exception of one bimane, we did not find any co-inclusion effects on the fluorescence of the complex solutions.

For the bimane family, the fluorescence of syn-(CH_3,CH_3) bimane, syn-(CH_3COOH_2,CH_3)bimane and syn-(C_6H_5,Cl) bimane wss examined. For the former two compounds, the effect of 10^{-2} M B-CD on the fluorescence of the guest compound was not altered by the presence of small amounts (1-2%) of ethanol. For syn-(C_6H_5,Cl)bimane, the bimane-ethanol-B-CD solution showed enhanced fluorescence as compared to the bimane-B-CD solution.

In the xanthene family, the effects on fluorescence of the possible co-inclusion of ethanol together with the guest compounds in the B-CD cavity were examined for the dyes rhodamine B and 6G as well as the disodium salt of fluorescein. In all cases, the presence of 1% ethanol together with 10^{-2} M B-CD had essentially the same effect as thst of 10^{-2} M B-CD alone.

Coumarins 102 and 153 were examined for possible co-inclusion of ethanol as well as methanol in the B-CD cavity. After rigorous exclusion of solubility effects, 1-2% of either of these alcohols had no effect on the fluorescence of these coumarins.

8. INFRA RED STUDIES OF CYCLODEXTRIN SOLID COMPLEXES WITH COUMARINS

Solid complexes, 1:1 molar ratio, were prepared from B-CD and coumarin, 7-hydroxycoumarin and the sodium salt of 7-hydroxy-4-methylcoumarin. These complexes could be recrystallized from water. Infra red (IR) spectra were taken in KBr and in Nujol. Marked shifts (15-50 cm^{-1}) were observed for the carbonyl signals upon comparison of the parent coumarins snd their B-CD complexes. It is noted that B-CD does not show any absorption in the carbonyl region. Likewise, KBr spectra of hydroxyethyl-B-CD (average moleculsr substitution 1 and 1.6) and of hydroxypropyl-B-CD (average molecular substitution 0.6 and 0.9) are very similar to spectra of B-CD and show no absorption in the carbonyl region. Solid complexes were prepared in 1:1 ratios of coumarin:CD using the above mentioned substituted cyclodextrins. Various methods of recrystallization were attempted, but only powders, very fine needles and in some instrances, gums, could be obtained which were unsuitable for single crystal X-ray diffraction analysis. IR analysis of the coumarin-B-CD complex had indicated a 20 cm^{-1} shift for the coumarin carbonyl. No such shift was noted for the coumarin:hydroxyethyl-B-CD MSl complex.

9. THIN LAYER CHROMATOGRAPHY OF LASER DYES WITH CYCLODEXTRINS IN THE MOBILE PHASE

The behavior of various laser dyes and dye analogs was examined by thin layer chromatography with various cyclodextrins added to the mobile phase. Different solid supports and mobile phases were utilized. In many instances, the addition of CDs to the mobile phase resulted in considerable increase in the retention factor value of the particular laser dye. These results may be of particular value in assessments of laser dye purity.

Coumarin laser dyes:

Five coumarin laser dyes, C30, C314, C314T, C102 and C153 were examined on polyamide TLC plates. An aqueous solution of urea and cyclodextrin was used as the mobile phase. B-CD and hydroxyethyl and hydroxypropyl CDs were examined. In all cases the presence of the CD increased the retention factor (Rf) value (Rf = distance coumpound travels/distance solvent travels). Overall, for this coumarin family, hydroxypropyl-B-CD was most effective in increasing Rf values. The coumarins listed above did not move at all on C18 reverse phase plates with mobile phases consisting of aqueous 4.0 M urea, 5% v/v t-butyl alcohol, 0.5 M NaCl and 0.1 M CD. The CDs examined as reverse phase mobile additives were B-CD and hydroxypropyl-B-CD MS=0.9. These coumarins have very similar Rf values on silica gel plates with ethanol as the mobile phase. Aqueous solutions of urea and CDs, however, allow for distinguishing these coumarins on silica gel plates. These results are summarized in Table 9.

Bimane laser dyes:

Five bimane dyes, syn-and anti-(Me,Me), syn-and anti-(Me,Cl), and syn-(Ph,Cl) were studied. TLC was carried out on polyamide and reverse phase C18 plates as described above. The presence of CDa does not make any significant difference in the Rf values obtained for these bimanes. The presence of CDs does not offer any particular advantage in the separation of the bimanes on silica gel plates as well. These results are summarized in Table 10.

Rhodamine laser dyes:

The rhodamine laser dyes, Rh6G and RhB as well as sulforhodamine B and Sulforhodamine 101 were examined on polyamide TLC plates as described above. In all cases, except for sulforhodamine 101, the addition of CDs to the mobile phase increased the Rf values of the rhodamines. In contrast, when reverse phase C18 plates were used, the addition of B-CD or hydroxypropyl-B-CD MS=0.9 to the mobile phase described earlier, had no significant effect on the Rf values. Examination of these dyes on silica gel plates with

aqueous urea and CDs in the mobile phase, revealed a marked increase for the Rf values in the presence of CDs. These results are summarized in Table 11.

Other heterocycles

A number of compounds were chosen from other heterocyclic systems to explore the scope of this method. The results are shown in Table 12.

2,5-diphenyloxazole: Does not move on polyamide or reverse phase C18 plates with or without CD.

fluorescein: Rf values are slightly increased by CDs in the nobile phase both on polyamide and reverse phase C18 plates. Rf values are increased by CDs in the mobile phase on silica plates.

indole: Rf values are increased by CDs in the mobile phase for polyamide, reverse phase C18 and silica gel plates.

TABLE 9

Rf Values of Coumarin laser dyes on polyamide TLC plates with aqueous 4.0M Urea mobile phases containing 10^{-1}M substituted and unsubstituted Betacyclodextrins

Coumarin dye	B-CD	HE*MS=1	HE*MS=1.6	HP*MS=0.6	HP*MS=0.9	Urea only
C30	0.94	0.76	0.65	1	0.76	0.05
C314	0.43	0.39	0.42	0.45	0.46	0.05
C314T	0.23	0.34	0.37	0.42	0.42	NM
C102	0.08	0.17	0.24	0.21	0.25	NM
C153	0.02	0.06	0.06	0.07	0.10	NM

Rf values of Coumarin laser dyes on silica gel TLC plates with aqueous 4/0 M urea mobile phases containing 10^{-1} M substituted and unsubstituted Betacyclodextrins

Coumarin dye	B-CD	HE*MS=1	HE*MS=1.6	HP*MS=0.6	HP*MS=0.9	Urea	Ethanol
C30	0.80	0.65	0.56	0.70	0.51	0.02	0.63
C102	0.24	0.49	0.51	0.48	0.54	0.03	0.61
C153	0.01	0.05	0.08	0.05	0.12	NM	0.62
C314	0.71	0.66	0.64	0.70	0.64	0.06	0.58
C314T	0.27	0.44	0.44	0.51	0.47	NM	0.62

B-CD: Beta cyclodextrin
HE*MS=1 and HE*MS=1.6: Hydroxyethyl Betacyclodextrin with average molecular substitution of 1 and 1.6 respectively
HP*MS=0.6 and HP*MS=0.9: Hydroxypropyl Betacyclodextrin with average molecular substitution of 0.6 and 0.9 respectively

NM: no movement

TABLE 10

Rf Values of bimane laser dyes on polyamide TLC plates with aqueous 4.0M Urea mobile phases containing 10^{-1}M substituted and unsubstituted Betacyclodextrins

bimane dye	B-CD	HE*MS=1	HE*MS=1.6	HP*MS=0.6	HP*MS=0.9	Urea only
syn(Me,Me)	0.94	0.90	0.74	1	0.91	0.90
anti(Me,Me)	0.70		0.68		0.68	0.62
syn(Me,Cl)	0.66	0.65	0.70	0.72	0.66	0.67
anti(Me,Cl)	0.45		0.41	0.43	0.44	0.37
syn(Ph,Cl)	0.05	0.04	0.05	0.05	0.06	NM

Rf values of bimane laser dyes on reverse phase C_{18} TLC plates with aqueous 4.0M urea mobile phases containing 5% v/v t-butyl alcohol, 0.5M NaCl and 0.1M cyclodextrin (Betacyclodextrin or hydroxypropyl Betacyclodextrin average molecular substituition of 0.9)

Bimane dye	B-CD	HP*MS=0.9	No CD
syn(Me,Me)	0.37	0.47	0.41
anti(Me,Me)	0.13	0.08	0.15
syn(Me,Cl)	0.45	0.45	0.43
anti(Me,Cl)	0.15	0.10	0.15
syn(Ph,Cl)	NM	NM	NM

Rf values of Bimane laser dyes on silica gel TLC plates with aqueous 4.0 M urea mobile phases containing 10^{-1} M substituted and unsubstituted Betacyclodextrins

Bimane dye	B-CD	HE*MS=1	HE*MS=1.6	HP*MS=0.6	HP*MS=0.9	Urea	Ethanol
Syn(Me,Me)	0.39	0.45	0.47	0.47	0.54	0.35	0.58
Anti(Me,Me)	0.64	0.65	0.65	0.63	0.68	0.55	0.72
Syn(Me,Cl)	0.39	0.43	0.49	0.48	0.52	0.35	0.65
Anti(Me,Cl)	0.42	0.44	0.43	0.48	0.46	0.33	0.72
Syn(Ph,Cl)	0.02	0.03	0.03	0.04	0.04	NM	0.68

B-CD: Beta cyclodextrin
HE*MS=1 and HE*MS=1.6: Hydroxyethyl Betacyclodextrin with average molecular substitution of 1.0 and 1.6 respectively
HP*MS=0.6 and HP*MS=0.9: Hydroxypropyl Betacyclodextrin with average molecular substitution of 0.6 and 0.9 respectively
NM: no movement

TABLE 11

Rf values of Rhodamine laser dyes on polyamide TLC plates with aqueous 4.0 M urea mobile phases containing 10^{-1} M substituted and unsubstituted Betacyclodextrins

Rhodamine dye	B-CD	HE*MS=1	HE*MS=1.6	HP*MS=0.6	HP*MS=0.9	Urea Only
RhB	0.97	0.91	0,92	0.92	0.96	0.37
Sulfo RhB	0.35	0.2*	0.25	0.33	0.27	0.07
Rh6G	0.64	0.58	0.52	0.52	0.68	0.43
Sulfo Rh101	0.03	0.03	0.05	0.03	0.04	0.04

Rf values of Rhodamine laser dyes on reverse phase C_{18} TLC plates with aqueous 4 M urea mobile phases containing 10^{-1} M substituted and unsubstituted Betacyclodextrins and 5% v/v t butyl alcohol, 0.5 M HaCl, and 0.1 M cyclodextrin

Rhodamine dye	B-CD	HP*MS=0.9	Urea Only
RhB	0.26	0.02	0.02
Sulfo RhB	0.26	0.27	0.05
Rh6G	NM	NM	NM
Sulfo Rh101	0.03	0.05	0.02

Rf values of Rhodamine laser dyes on silica gel TLC plates with aqueous 4.0 M urea mobile phases containing 10^{-1} substituted and unsubstituted Betacyclodextrins

Rhodamine B dye	B-Cd	HE*ME=1	HE*MS=1.6	HP*MS=0.6	HP*MS=0.9	Urea Only	Acetone
Rhodamine B	0.57	0.51	0.40	0.45	0.46	0.08	0.26
Sulfo rhodamine B	0.79	0.67	0.64	0.68	0.72	0.28	0.02
Rhodamine 6G	0.33	0.24	0.25	0.28	0.25	0.10	0.06
Sulfo rhodamine 101	0.25	0.34	0.38	0.36	0.47	0.22	NM

B-CD: Beta cyclodextrin
HE*MS=1 and HE*MS=1.6: Hydroxyethyl Betacyclodextrin with average molecular substitution of 1 and 1.6 respectively
HP*MS=0.6 and HP*MS=0.9: Hydroxypropyl Betacyclodextrin with average molecular substitution of 0.6 and 0.9 respectively
NM: no movement

TABLE 12

Rf Values of indole, 2,5-diphenyloxazole, and fluorescein on polyamide TLC plates with aqueous 4.0M Urea mobile phases containing 10^{-1}M substituted and unsubstituted Betacyclodextrins

Compound	B-CD	HE*MS=1	HE*MS=1.6	HP*MS=0.6	HP*MS=0.9	Urea only
2,5 diphenyl-oxazole	NM	NM	NM	NM	NM	NM
fluorescein	0.07	0.14	0.14	0.20	0.19	NM
Indole	0.36	0.37	0.37	0.42	0.42	0.05

Rf values of indole, 2,5-diphenyloxazole and fluorescein on reverse phase C_{18} TLC plates with aqueous 4.0M urea mobile phases containing 5% v/v t-butyl alcohol, 0.5M NaCl and 0.1M cyclodextrin (Betacyclodextrin or hydroxypropyl Betacyclodextrin average molecular substituition of 0.9)

Compound	B-CD	HP*MS=0.9	No CD
2,5-diphenyloxazole	NM	NM	NM
Fluorescein	0.09	0.22	NM
Indole	NM	0.18	NM

Rf values of indole and fluorescein on silica gel TLC plates with aqueous 4.0 M urea mobile phases containing 10^{-1} M substituted and unsubstituted Betacyclodextrins

Compound	B-CD	HE*MS=1	HE*MS=1.6	HP*MS=0.6	HP*MS=0.9	Urea	Ethanol
fluorescein	0.49	0.64	0.63	0.66	0.72	0.09	0.63
indole	0.44	0.50	0.46	0.49	0.51	0.09	0.06

B-CD: Beta Cyclodextrin
HE*MS=1 and HE*MS=1.6: Hydroxyethyl Betacyclodextrin with average molecular substitution of 1 and 1.6 respectively
HP*MS=0.6 and HP*MS=0.9: Hydroxypropyl Betacyclodextrin with average molecular substitution of 0.6 and 0.9 respectively

NM: no movement

10. EXTRACTION OF LASER DYES FROM AQUEOUS SOLUTION WITH SOLID PHASE EXTRACTION CYCLODEXTRIN CARTRIDGES

Solid phase extraction cartridges (SPE cartridges) packed with silica bonded CDs were examined as a potential means of purification and/or extraction of aqueous solutions of laser dyes. Extraction using alpha, beta and gamma CD containing cartridges was compared to C18 cartridges.

Initially, extraction with B-CD SPE cartridges was studied using 10 ml samples of aqueous solutions of coumarins 101, 314, 314T, 30 and 153 as well as coumarin, indole and syn(Me,Me)bimane. Complete extraction was achieved for all these compounds, except for syn(Me,Me)bimane. Washing the cartridge with water, caused coumarin, indole and the bimane to be eluted from the cartridge. For all compounds except the bimane, good or near quantitative recovery of the compound from the SPE cartridge could be achieved by elution with methanol-chloroform-ethanol. The presence of the compounds was monitored by UV absorption. Pilot studies indicate that reuse of the B-CD cartridges is possible. These results are summarized in Table 13.

Further studies comparing alpha, beta, gamma-CD and C18 SPE cartridges were carried out using 50 ml samples of 10^{-5}M coumarin 30 and 153 as well as coumarin and indole. Complete extraction of coumarins 30 and 153 was achieved with good to excellent recovery of these compounds from the cartridges using elution with methanol, chloroform-ethanol, and acetonitrile solvents. Both UV absorption and fluorescence emission was used to monitor the presence of these compounds. Under the conditions used for this experiment, no particular advantage could be noted for one cartridge over another. For coumarin and indole, however, extraction efficiency was poor and most of each compound passed through the cartridges without being retained. These results are summarized in Table 14.

TABLE 13

EXTRACTION OF LASER DYES AND ANALOGS FROM AQUEOUS SOLUTIONS
(Monitored By UV Absorption)

USING BETA-CYCLODEXTRIN BONDED SOLID PHASE EXTRACTION CARTRIDGES

Compound	Extraction Efficiency	Water Wash	Organic Eluate	Reconstituted Sample	Cartridge History
C102, 10^{-5}M	complete for 10 ml	No cpd washed out	Cpd eluted	Good recovery	New, reused 1x, reused 2x
C314, 10^{-5}M	complete for 10 ml	No cpd washed out	Cpd eluted	Good recovery	New, reused 1x, reused 2x
C314T, 10^{-4}M	complete for 10 ml	No cpd washed out	Cpd eluted	Good recovery	New, reused 1x
C30, 10^{-5}M	complete for 10 ml	No cpd washed out	Cpd eluted	Good recovery	New
C153, 10^{-5}M	complete for 10 ml	No cpd washed out	Cpd eluted	Near Quant. recovery	New
Coumarin 10^{-5}M	complete for 10 ml	Cpd washes out	Unwashed cpd eluted	Near Quant. recovery	New
Indole 10^{-5}M	complete for 10 ml	Cpd washes out	Unwashed cpd eluted	Good recovery	New
syn(Me,Me) bimane 10^{-5}&10^{-3}M	incomplete retention for 10 ml	Cpd washes out			New

TABLE 14

Extraction of Laser Dyes (and analogs) from Aqueous Solution using Cyclodextrin and C18 Solid Phase Extraction Cartridges

SPE cartridge:	α-CD	B-CD	γ-CD	C18 unconditioned	C18 preconditioned
Compound: Coumarin 30, 10^{-5}M, 50 ml sample					
Extraction Efficiency[a] :	complete	complete	complete	complete	complete
Recovery from Cartridge[a] :	excellent	excellent	excellent	good	excellent
Compound: Coumarin 153, 10^{-5}M, 50 ml sample					
SPE cartridge:	α-CD	B-CD	γ-CD	C18 unconditioned	C18 preconditioned
Extraction Efficiency[a] :	complete	complete	complete	complete	complete
Recovery from Cartridge[a] :	good	good	excellent	good	excellent
Compound: Coumarin, 10^{-5}M, 50 ml sample					
SPE cartridge:	α-CD	B-CD	γ-CD	C18 unconditioned	C18 preconditioned
Extraction Efficiency[b] :	poor	poor	poor	poor	poor
Recovery from Cartridge[b] :	----	----	----	----	----
Compound: Indole, 10^{-5}M, 50 ml sample					
SPE cartridge:	α-CD	B-CD	γ-CD	C18 unconditioned	C18 preconditioned
Extraction Efficiency[b] :	poor	poor	poor	poor	poor
Recovery from Cartridge[b] :	----	----	----	----	----

a. Monitored by UV absorption and fluorescence emission
b. Monitored by UV absorption

REFERENCE PUBLICATIONS

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